U.S. Department of Energy
Energy Efficiency and Renewable Energy

biomass program

Cleanup and Conditioning Project
Integrated Catalyst Studies Task

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Presentation Outline

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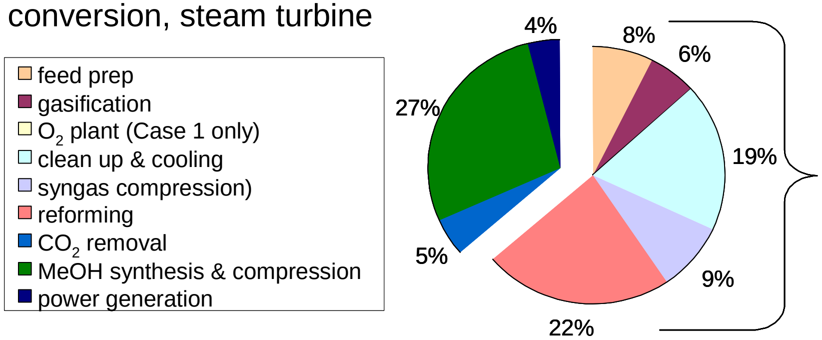
Project Background

Case 2 - Indirect: BCL, scrubbing, steam reformer, shift, MeOH conversion, steam turbine



Clean, reformed syngas generation = 60-64% of total capital in the TC component of Integrated Biorefinery

- Technoeconomic analysis has shown that cleanup and conditioning of biomass-derived syngas has the greatest impact on the cost of clean syngas.
- Gas cleanup and conditioning technologies and systems are unproven in integrated biorefinery applications.
- Chemical contaminants in biomass-derived syngas: tar, ammonia, chlorine, sulfur, alkali metals, and particulates
- Gas cleanup and conditioning strategies based on catalytic reforming to convert tars and produce a clean syngas from a range of biomass feedstock.
- Catalytic steam reforming of biomass gasification tars is being demonstrated using commercial and developing catalysts.

Pathways and Milestones – C-level and Project Milestones

Ag Residues	Perennial Grasses / Woody Crops	Pulp and Paper	Forest Products
Validate Cost-effective Gas Cleanup Performance			
M 4.11.3 M 4.12.3	M 5.11.3 M 5.12.3	M 6.3.4	M 7.1.4
Validate integrated gasification and gas cleanup at pilot scale			
M 4.11.5 M 4.12.5	M 5.11.5 M 5.12.5	M 6.3.5	M 7.1.5

Project Milestones	Type	Performance Expectations	Due Date
Test 3 best catalysts for fluidized bed tar reforming applications using base wood feedstock and selected biorefinery residue	D	An integrated approach to optimize tar reforming for biorefinery residue gasification will combine the results from microactivity tests, slip-stream catalyst performance evaluation, and full stream extended catalyst evaluation to determine the most robust catalysts with highest activities and longest lifetimes that have potential for use in future regenerating tar reforming applications	Sept. 2005
Extended Pilot-Scale Catalyst Lifetime Studies	D	More than 200 hr on-line catalytic steam reforming of tars in syngas derived from the biorefinery residues	Sept. 2006

Technical Feasibility and Risks

- Commercial catalysts for Steam Methane and Naphtha reforming
- Developing reforming catalysts for fuel cell applications
- Pilot-scale demonstration of integrated gasification/tar reforming – gasifier outlet T vs. reformer inlet T
- Challenge: stringent gas cleanup requirements for complex and variable syngas

Syngas Impurities and Tolerances for Fuels Synthesis

	Level	**Source**
Particulate	0 > 2 µm	Tijmensen, *et al.* 2002
Tar	0 ppm	Jackson, *et al.* 1995
Sulfur	0.2 ppm	Dry, 1981
	1 ppmv	Boerrigter, *et al.* 2002
	60 ppb	Turk, *et al.* 2001
Halides	10 ppb	Boerrigter, *et al.* 2002
Nitrogen	10 ppmv NH_3 0 ppmv NOx 10 ppb HCN	Turk, *et al.* 2001

Competitive Advantage

	Advantages	*Disadvantages*
Wet Scrubbing	• Proven technology for large scale • Economy of scale • Commercially available • Tar byproducts	• If tars are not recycled –Aqueous waste stream –Loss of tar fuel value • Thermodynamic efficiency losses • “Product” separation
Catalytic Steam Reforming	• Improved heat integration w/ gasifier • Improved C conversion • Reforming & Shift conversion	• Developing technology • Catalyst lifetime • Catalyst cost?

Project Overview

Stage Placement – Stage B

Build upon exploratory knowledge in a focused, detailed experimental program. Not directly related to commercialization but knowledge or capability is used in new or existing commercially focused projects.

Project Objective

Remove contaminants from raw biomass syngas to meet the gas cleanliness requirements of commercial and developing fuels, chemicals, and heat & power processes

Impact of Thermochemical Platform in Integrated Biorefinery

Transition from testing 5 catalysts with wood derived-syngas to 3 catalysts with corn stover-derived syngas compared to performance with wood-derived syngas

Technical Goals

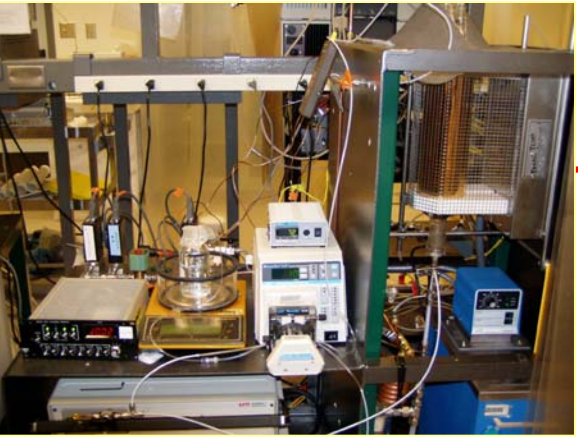
- Deactivation kinetics
- Steady-state conversion efficiency
- Bench and pilot-scale efforts aligned to determine optimized reforming catalyst performance
- Provide technical data for design of regenerating tar reforming reactor and refined technoeconomic analyses

Tar Reforming Catalyst Development

MATS 1

- Fixed bed 1 g catalyst
- Catalyst characterization
- Temperature programmed reaction

Rapid catalyst preparation



MATS 2

- Fixed bed 1 g catalyst
- Tar destruction
- Liquid reforming
- TCPDU slipstream

2" FBR

- Fluid bed 250 g catalyst
- Kinetic data
- Lifetime data
- TCPDU slipstream
- Comprehensive online analysis

TCPDU

- Fluid bed 50 kg catalyst
- Process data
- Kinetic data
- Lifetime data
- Comprehensive online analysis

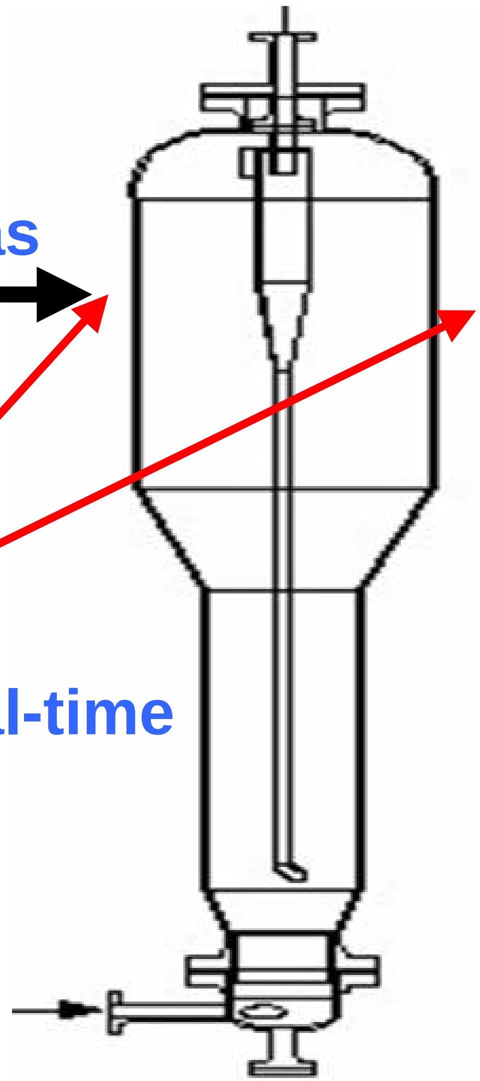
Multivariate Models

- Guide catalyst optimization

Full-stream Reforming in the NREL TCPDU

Raw Syngas

Clean Syngas



Comprehensive, real-time syngas analysis

Compound	Goal
Methane (CH_4)	80%
Ethane (C_2H_6)	99%
Ethylene (C_2H_4)	90%
Tars (C_{10+})	99.9%
Benzene (C_6H_6)	99%
Ammonia (NH_3)	90%

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On-line, Real-time MBMS Tar Sampling

Molecular Weight	Formula	Chemical Name(s)
15,16	CH_4	methane
26	C_2H_2	acetylene
78	C_6H_6	benzene
91,92	C_7H_8	toluene
94	C_6H_6O	phenol
104	C_8H_8	styrene
106	C_8H_{10}	(m-, o-, p-) xylene
108	C_7H_8O	(m-, o-, p-) cresol
116	C_9H_8	indene
118	C_9H_{10}	indan
128	$C_{10}H_8$	naphthalene
142	$C_{11}H_{10}$	(1-, 2-) methylnaphthalene
152	$C_{12}H_8$	acenapthylene
154	$C_{12}H_{10}$	acenaphthene
166	$C_{13}H_{10}$	fluorene
178	$C_{14}H_{10}$	anthracene, phenanthrene
192	$C_{15}H_{12}$	(methyl-) anthracenes/phenanthrenes
202	$C_{16}H_{10}$	pyrene/fluoranthene
216	$C_{17}H_{12}$	methylpyrenes/benzofluorenes
228	$C_{18}H_{12}$	chrysene, benz[a]anthracene, …
242	$C_{19}H_{14}$	methylchrysenes, methylbenz[a]anthracenes
252	$C_{20}H_{12}$	perylene, benzo[a]pyrene, ...
266	$C_{21}H_{14}$	dibenz[a,kl]anthracene, …
278	$C_{22}H_{14}$	dibenz[a,h]anthracene, …

Advantages

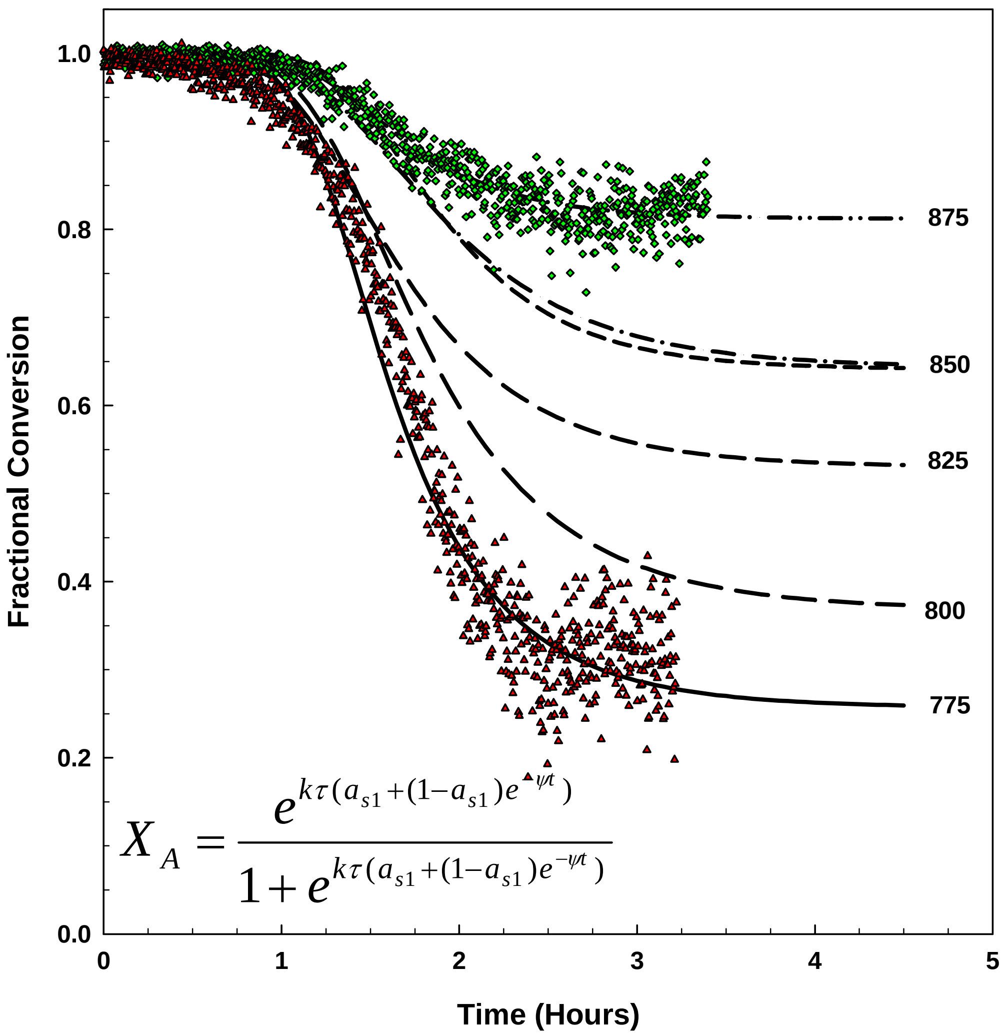
- Universal detection (low and high molecular weight species)
- Real-time monitoring
- Preserves reactive and condensable species
- Rapid screening/fingerprinting
- Large dynamic range (10^6 to 10^{-1} ppmv)
- High-pressure, high-temperature system monitoring

History and Accomplishments

- FY04 – Slipstream tar reforming studies for fundamental deactivation kinetics of NREL23 catalyst with wood-derived syngas
  - Initial deactivation and steady-state conversion (5T, 1τ)
  - Submitted for publication I&ECR
- FY04 – Full-stream tar reformer installation and operation
  - Initial deactivation and steady-state conversion (3T, 3τ)
- FY05 – Refocused Thermochemical Platform
  - Full-stream catalyst studies comparing tar conversion efficiency of 3 catalysts with wood- and corn stover-derived syngas (FY05 milestone 9/05)
    - Baseline parametric corn stover gasification studies (complete)
    - NREL23 – wood and corn stover syngas (complete)
    - NREL14 – wood and corn stover syngas (wood complete, CS this week)
    - NRELX – wood and corn stover syngas (TBD)

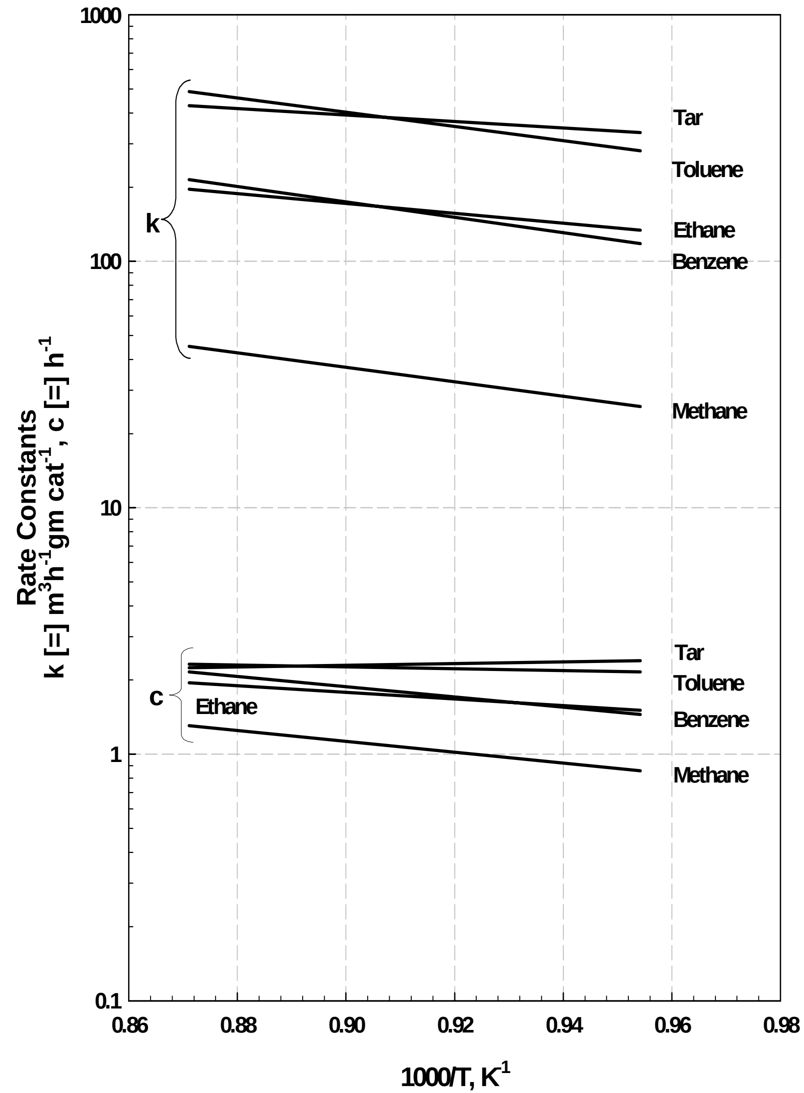
FY04 Summary
Slipstream Catalyst Deactivation Kinetics

Benzene Fractional Conversion, N1D1 Model



$$X_A = \frac{e^{k\tau(a_{s1}+(1-a_{s1})e^{-\psi t})}}{1+e^{k\tau(a_{s1}+(1-a_{s1})e^{-\psi t})}}$$

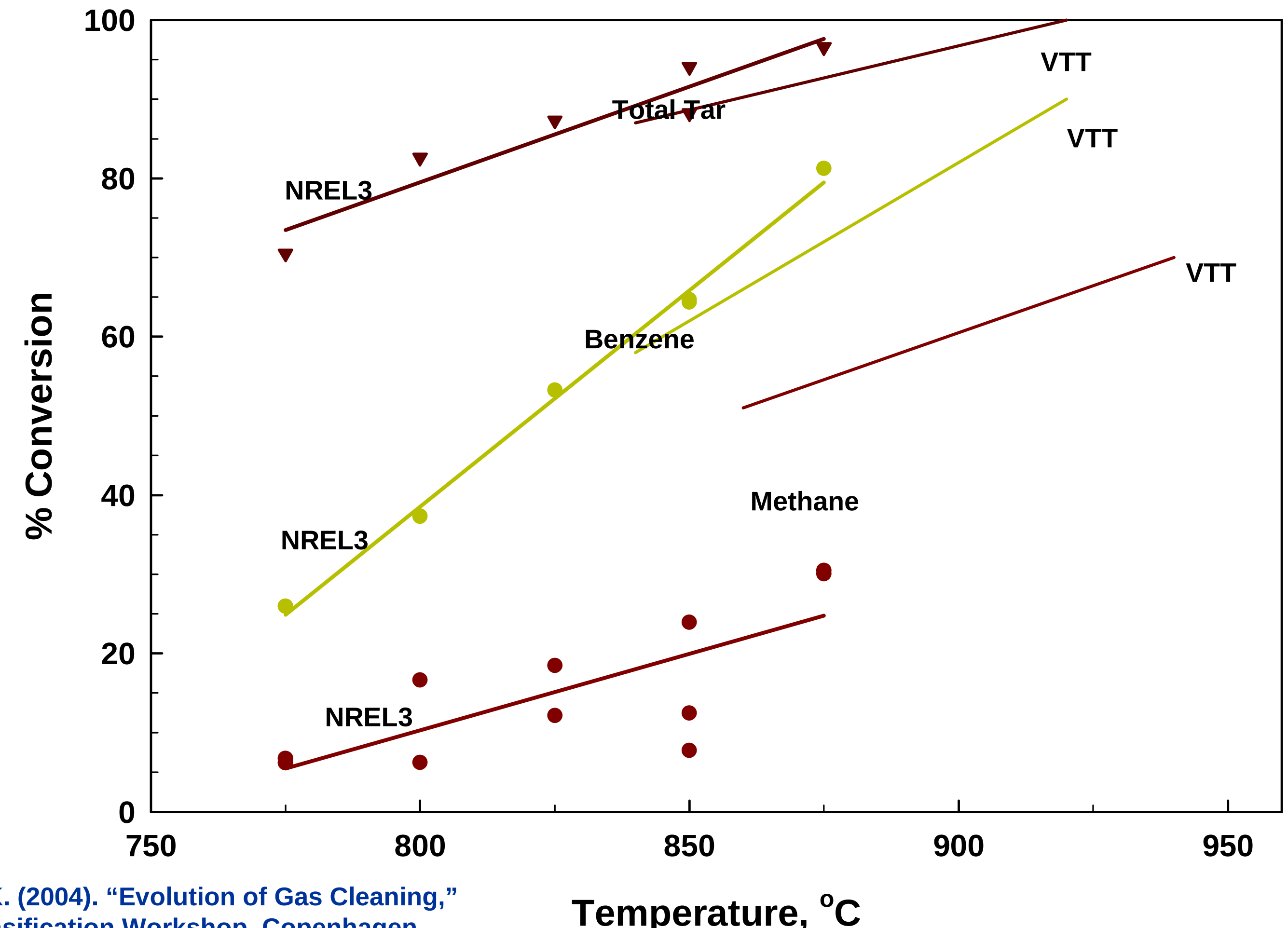
N1D1 Model Arrhenius Plots



Steady-State Conversion Versus Temperature

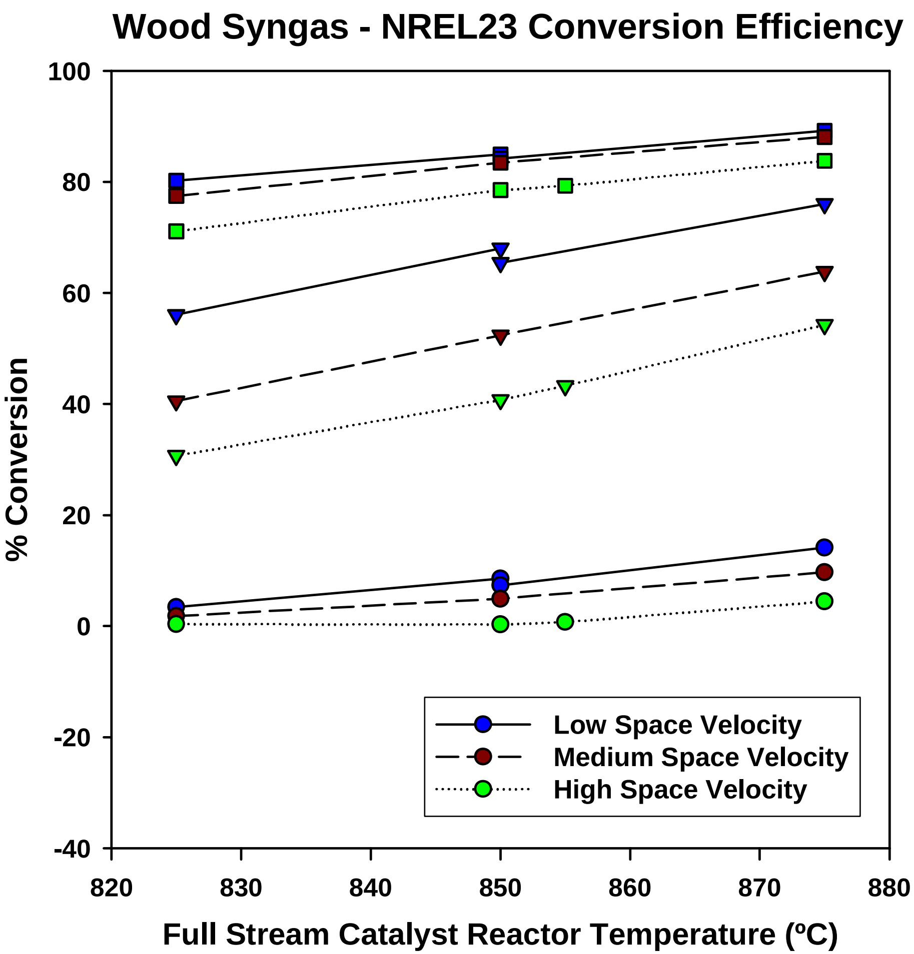
Reported Tar, Benzene Methane Conversions

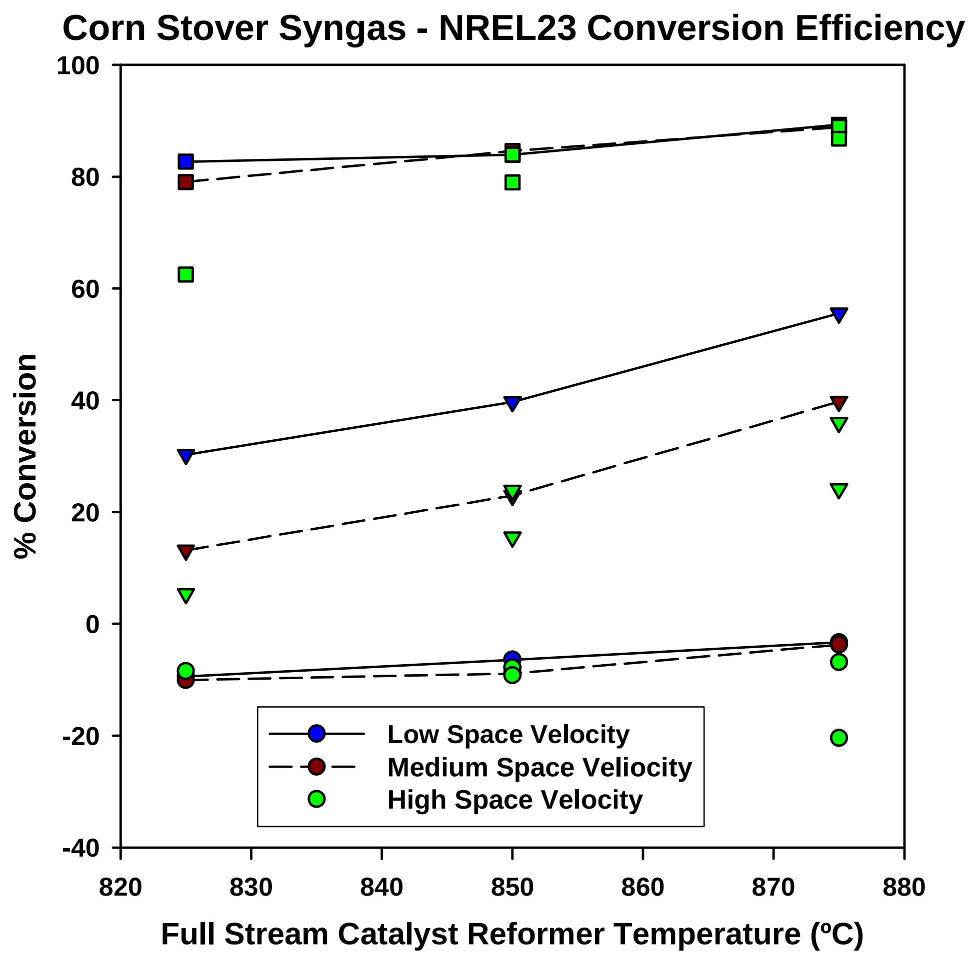
NREL23 Catalyst (Short Term Steam Gasification)
VTT Monolithic Catalyst (Long Term POX Gasification)



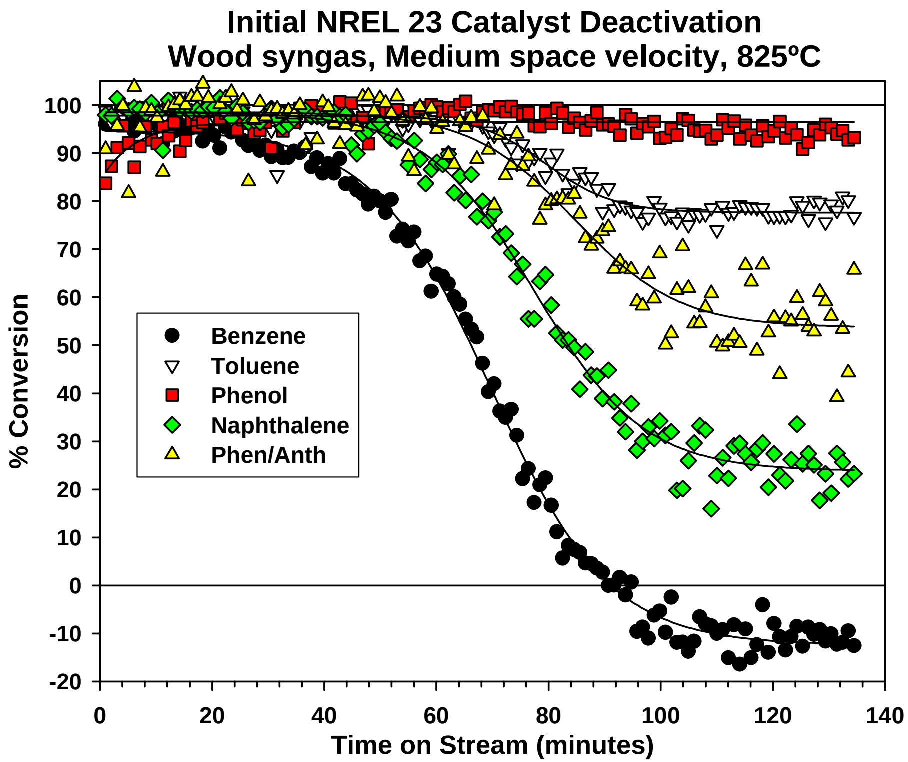
Ref. For VTT Data: Salo, K. (2004). "Evolution of Gas Cleaning," IEA Bioenergy Task 33 Gasification Workshop, Copenhagen, Denmark, Oct 25.

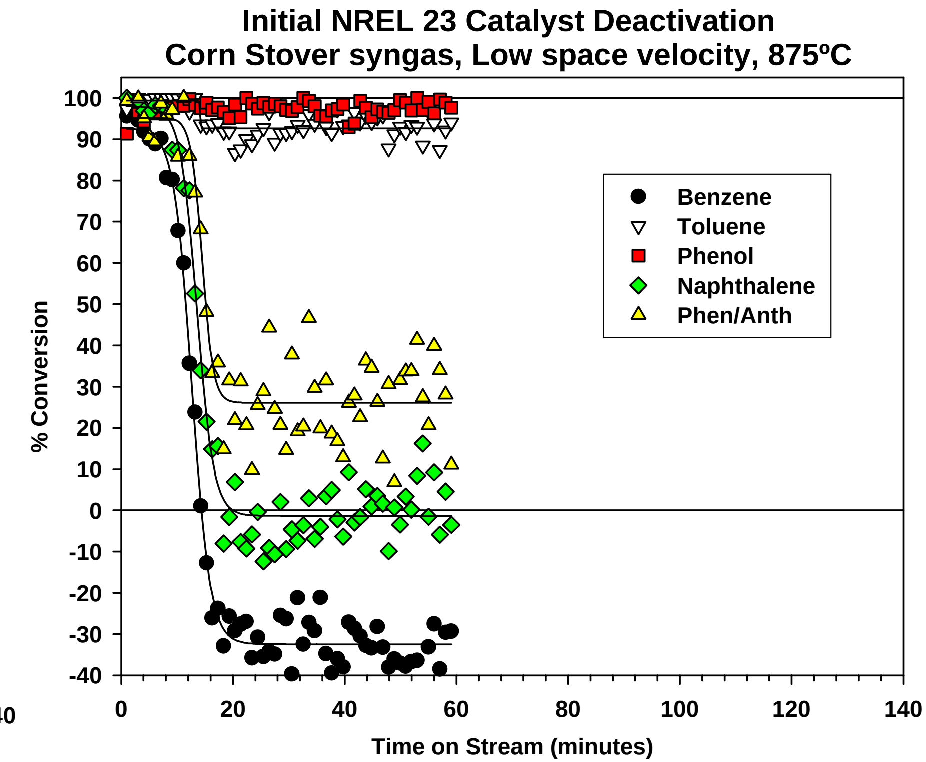
FY05 Results
Comparison of Catalyst Performance as a Function of Syngas Composition





FY05 Results
Comparison of Initial Catalyst Deactivation as a Function of Syngas Composition





Plan/Schedule

FY05

- Complete NREL14 catalyst testing with corn stover syngas (6/10/05)
- Select 3rd catalyst based on results of Catalyst Development milestone (6/30/05)
- Catalyst testing with selected catalyst with wood and corn stover syngas (8/15/05)
  - Initial deactivation and steady-state activities
- Evaluate alternative supports
- Milestone Completion Report – 9/30/05

FY06

- Long-term catalyst lifetime testing (greater than 200hr) with best performing catalyst
- Design regeneration systems for maintaining long-term activity of the tar cracking catalysts
- Design and install sulfur mitigation unit operation in TCPDU
- Tar reforming studies with syngas from lignin-rich residue
- Partnership Development: Evaluate alternative reforming catalysts

Critical Issues and Show-stoppers

- Implementing available sulfur removal technology sooner rather than later
- On-line Sulfur and Nitrogen measurements
  - Impact of sulfur concentration on catalyst performance (near and long-term)
  - NH_3 and HCN conversion efficiencies
- Effect of support composition on catalyst performance (activity and attrition)
- Optimized catalyst formulation

Summary

- Full stream, pilot-scale studies – 3 catalysts, 2 feedstocks (wood and corn stover syngas)
- Correlate with bench-scale results to optimize catalyst performance
- Potential impact of syngas sulfur content on reforming catalyst performance
  - Sulfur tolerant catalysts
  - Sulfur removal technologies
- Provide an integrated biomass gasification/catalyst testing facility for integrated biorefinery developers
  - Different feedstocks with specific catalysts
  - Developing catalysts with known feedstocks
- Implications of measured catalyst performance
  - Regenerating catalyst reactor design
  - Revised/refined technoeconomic analyses
- Funding History ($k): FY03 – 1,742   FY04 – 1,527   FY05 – 1,300

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NREL Thermochemical Group

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